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FROM: PROI (TI) (STINFO)

13 December 1999

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-TP-1999-0254**
Sheehy, Jeff, "Advanced Chemical Propellants: The HEDM Program" (BFI)

JANNAF Propulsion Meeting (Tucson, AZ, 14-16 Dec 1999) **(Statement A)**

Advanced Chemical Propellants:
The High Energy Density Matter Program

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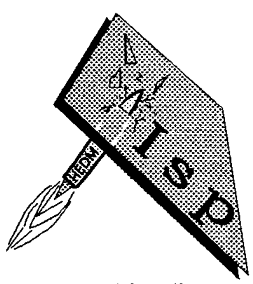
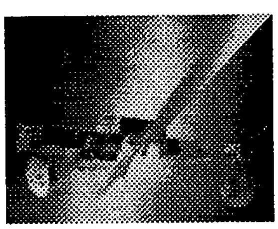
HEDM Program Objective

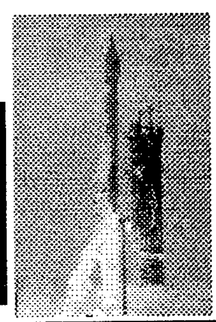
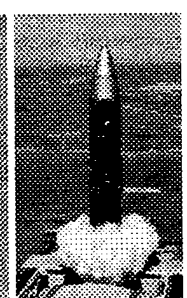


Breaking the performance barrier

Identify and develop advanced chemical propellants for rocket propulsion applications

- Hydrocarbons for liquid boosters
- Liquid & solid oxidizers for boost and upper stages
- Monopropellants for upper stages and satellites
- Cryogenic propellants for upper stages



Payoffs of HEDM Propellants

- Larger payloads, smaller vehicles, and lower launch costs
- Greater capability to access and exploit space

Vehicle Type	Baseline Vehicle	Propellant	Takeoff Mass (lb)	Payload Mass (lb)	Payload Mass (lb) With 10% Isp Increase
Two-stage ELV	Atlas G // Centaur D-1A	RP-1/LOX (Isp = 295 s) // LH2/LOX (Isp = 455 s)	360,000	12,500	15,600 **(+25%)**
SSTO RLV	Rockwell SSTO	LH2/LOX (Isp = 455 s)	1,900,000	40,000	68,000 **(+70%)**
Missile Defense Interceptor	Boost-Phase Interceptor	HTPB/Al/HMX (Isp = 270 s)	1,847	74	110 **(+49%)**

HEDM research at AFRL is aimed at increasing propellant Isp by 5 to 50%

Types of Research Performed In the HEDM Program

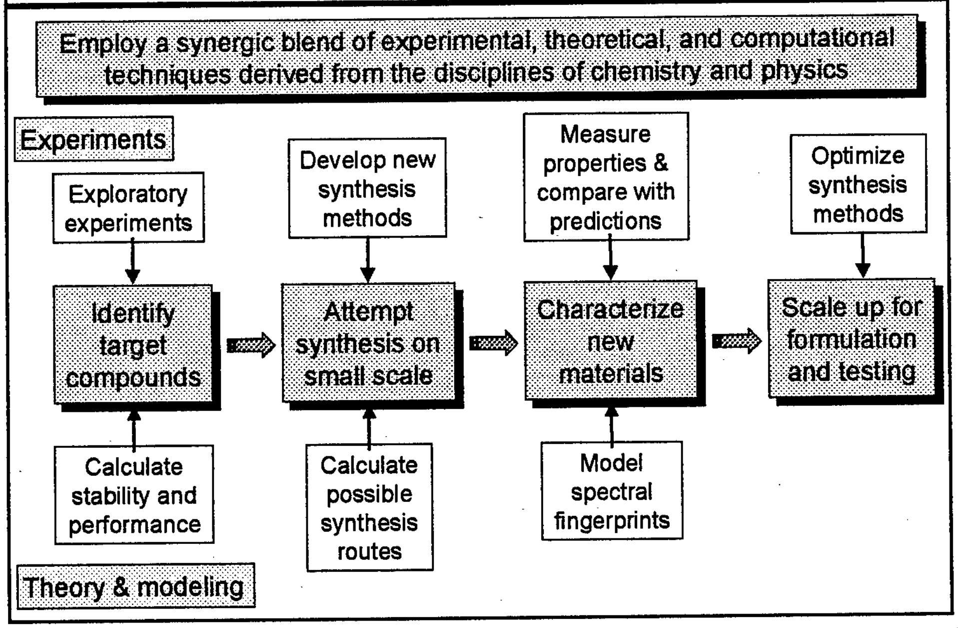
- Fundamental research -- done with little understanding of potential applications
- Strategic research -- resolve issues standing between knowledge and applications

- Basic research -- creates new knowledge
- Applied research -- creates new technologies

How these components relate to give a coherent HEDM R&D program:

	Fundamental	Strategic
Basic	Understanding and extending chemical & physical principles	Laboratory-scale synthesis of new molecules
Applied	Pilot-plant synthesis and subscale tests of new ingredients	Prototype propulsion system for new propellants

Approach To Developing HEDM Propellants



HEDM Program Resources Summary

Source	FY97	FY98	FY99	FY00
Man Years	11.1	10.5	10.5	11.5
6.2 Contribution	900	950	1000	1000
AFOSR Core (6.1)	529	464	595	395
AFOSR NWV (6.1)	254	197	275	275
Total AFOSR	783	661	870	670
NASA		200		
DARPA		193	491	500[a]
Total funding	**1683**	**2004**	**2361**	**2170[a]**

[a] Anticipated funding level.

All monetary values are in $ K.

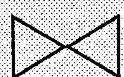
New Energetic Hydrocarbon Fuels

KEY ISSUES

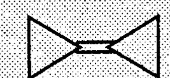
Can we discover and develop hydrocarbons with these characteristics:

- Higher theoretical performance (specific impulse) than RP-1
- Desirable physical properties (density, melting point, boiling point)
- Compatibility with existing engine hardware
- Synthesis routes that can be carried out economically on a large scale

Candidate HEDM fuels incorporate strain and unsaturation:



spiropentane



bicyclopropylidene

$HC{\equiv}C{-}CH_2{-}CH_2{-}C{\equiv}CH$

1,5-hexadiyne

	spiropentane	bicyclopropylidene	1,5-hexadiyne
Isp (sec; RP-1 = 299)	311	313	312

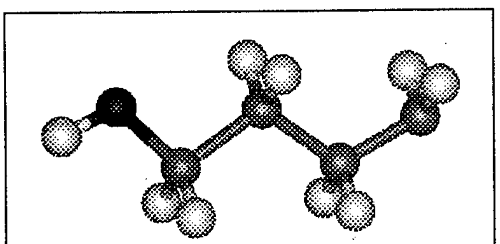
New Energetic Monopropellants

KEY ISSUES

Can we discover and develop monopropellants with these characteristics:

- Higher theoretical performance (specific impulse) than hydrazine
- Desirable physical properties (density, vapor pressure, thermal stability)
- No toxicity concerns (hydrazine is carcinogenic and dermally toxic)
- DOT Class 1.3 explosive (not Class 1.1)

Hardware (catalyst beds, nozzles, etc.) that will withstand the higher temperatures characteristic of energetic materials must be designed

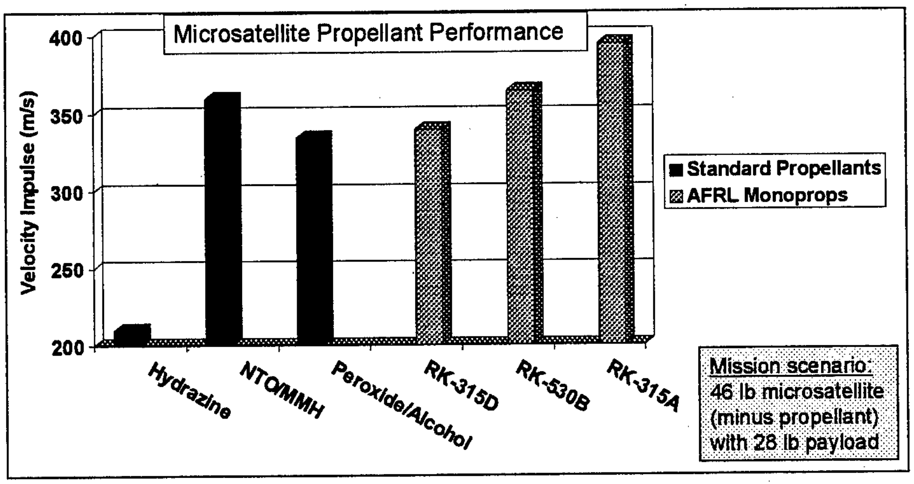


The nitrate, perchlorate, or dinitramide salts of hydroxyethylhydrazinium may yield monopropellants that are superior to hydrazine:

- 50% denser
- 25% higher Isp
- Much less toxic

Payoffs of Energetic Monopropellants

The performance of new advanced monopropellants can dwarf that of hydrazine, and can significantly exceed even bipropellant systems



Energetic Monopropellant Prospectus

Planned FY99	Accomplished FY99	Planned FY00
Synthesize several new ingredients for blended energetic monopropellants	Synthesized several new hydroxyethylhydrazinium, nitrocyanamide, and high-nitrogen heterocycle salts	Continue synthesis of new ingredients, with new emphasis on single-component ionic liquids
Deliver sufficient quantities of new ingredients for formulation and testing	Delivered several potential new ingredients to Propellant Development group for sensitivity testing and thruster firings	Continue interaction with Propellant Development group to obtain timely testing of potential new monopropellants
Synthesize compounds for an AFRL project to develop methods of predicting toxicities of candidate ingredients	Delivered several compounds to AFRL/HE (WPAFB) for toxicity studies	Complete the synthesis of prototypical compounds for this project

Discovery of New Polynitrogen Compounds

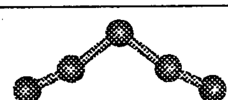
Program Objective: Synthesize and characterize new highly energetic polynitrogen compounds

Modeling and simulations directs the experimental program:

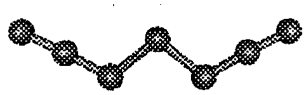
- Determines which molecules should exist and how energetic they are – what should we try to make?
  - ⇒ Calculate stationary points on potential-energy surfaces (minima and barriers to decomposition and reaction)
- Helps develop methods of synthesizing promising target molecules – how can we make it?
  - ⇒ Designing a reaction depends largely on the intuition of a clever synthesis chemist but it can be influenced by quantum-chemical calculations
- Identifies and characterizes new molecules – did the synthesis work?
  - ⇒ Compare measured properties with predictions from modeling and simulation to determine whether the desired compound was made

This project is co-sponsored by DARPA and AFOSR

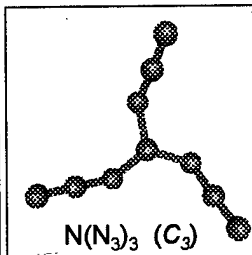
Calculations Suggest Which Unknown Polynitrogens Could Possibly Exist



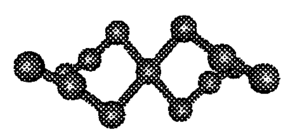
N_5^+ (C_{2v})



$N(N_3)_2^-$ (C_2)



$N(N_3)_3$ (C_3)



$N(N_3)_4^+$ (D_{2d})

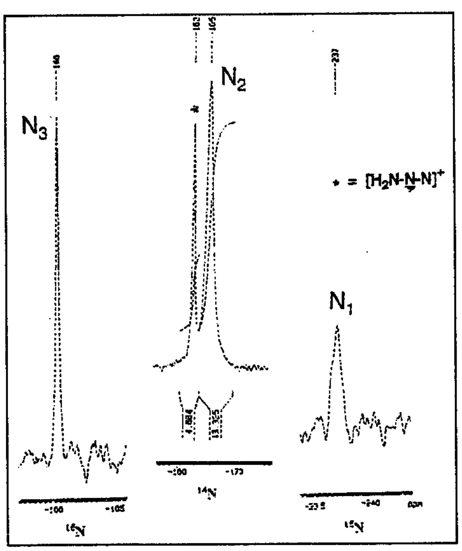
- We calculated that the compounds depicted above are all stable, albeit to varying extents, and highly energetic
- Further calculations on N_5^+ showed that the structure depicted is the global minimum on the potential surface, significantly more stable than $N_2 + N_3^+$ or $N_2^+ + N_3$, so it might be preparable from materials containing such components

Synthesis Route for N_5^+

- Preparing the starting materials:
  - ⇒ NaN_3 + stearic acid → HN_3 (at 80°C)
  - ⇒ Graphite + AsF_5 ⟶ $C_{10}{\bullet}AsF_5$
  - ⇒ 2 $C_{10}{\bullet}AsF_5$ + N_2F_4 ⟶ 2 $C_{10}^+AsF_6^-$ + *trans*-N_2F_2
  - ⇒ *trans*-N_2F_2 ⟶ *cis*-N_2F_2
  - ⇒ *cis*-N_2F_2 + MF_5 ⟶ $N_2F^+MF_6^-$ (M = As, Sb)
- Combining the starting materials:

$$N_2F^+MF_6^- + HN_3 \xrightarrow[-78°C]{HF} N_5^+MF_6^- + HF$$

Did The Synthesis Work? Did We Make N_5^+? Compare Calc. & Exptl. NMR Spectra



Predicting nitrogen NMR chemical shifts typically requires very intensive calculations that are infeasible for species like N_5^+

We devised a method of accounting for the most important physical effects with less demanding calculations:

$$\delta[\text{calc}] = \delta[\text{MP2/pz3}d\text{1}f] - \delta[\text{MP2/qzp}] + \delta[\text{CCSD(T)/qzp}]$$

NMR Chemical Shifts (ppm)†

Atom	Obs.	MP2‡	CCSD(T)‡	δ[calc]
N_1	-237.3	-180	-215	-236
N_2	-165.3	-85	-146	-167
N_3	-100.4	-80	-75	-88

† Relative to CH_3NO_2 ‡ qzp basis set

N_5^+ Salt in Low-Temperature Raman Spectrometer: Before and After Explosion

The New Polynitrogen N_5^+: The News Travels Far and Wide

The New York Times
ON THE WEB

February 2, 1999

New Nitrogen Ion Carries Warning: Handle With Care

By MALCOLM W. BROWNE

For a century, chemists doubted that such a substance could exist, but scientists at an Air Force laboratory have created a bizarre form of nitrogen believed to be one of the most violently explosive substances ever made.

To the astonishment of many other scientists, a team of chemists headed by Dr. Karl O. Christe and Dr. William W. Wilson at the Air Force Research Laboratory at Edwards Air Force Base, Calif., reported their achievement at a recent meeting of the American Chemical Society.

THE TIMES

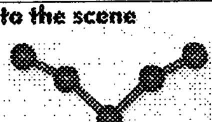
The next big bang: explosive the size of salt grains

The creation of N_5, an atomic freak of nature, has stunned the world of chemistry. Nicholas Booth reports

Chemistry in Britain

Exploding onto the scene

It may not be the safest compound to work with, but chemists from the Air Force Research Laboratory's propulsion directorate, based at Edwards Air Force Base in California, US, have recently managed to synthesise the first new all-nitrogen species for more than 100 years - a salt containing an N_5^+ cation



propellants, and the N_5^+ cation is reportedly a more powerful oxidiser than O_2^+ and reacts explosively

CPIA Bulletin

Breakthrough in Polynitrogen Chemistry

Polynitrogen Program Plan

- Synthesis of $N_2F^+SbF_6^-$ starting material:

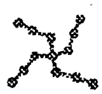
$$NiF_3^+SbF_6^- + N_2 \longrightarrow N_2F^+SbF_6^-$$

$$\Rightarrow \text{Graphite} \xrightarrow{+AsF_5} C_{10}\bullet AsF_5 \xrightarrow{+N_2F_4} trans\text{-}N_2F_2 \longrightarrow cis\text{-}N_2F_2 \xrightarrow{+SbF_5} N_2F^+SbF_6^-$$

- Synthesis of $N_5^+SbF_6^-$, then metathesis to form a neutral polynitrogen:

$$\Rightarrow N_2F^+SbF_6^- + HN_3 \longrightarrow \underset{\text{stability tests, safety tests}}{N_5^+SbF_6^-} \xrightarrow{\text{(x10) scale up}} \underset{\text{compatibility tests}}{N_5^+SbF_6^-} \xrightarrow{+N_3^-} \xrightarrow{\text{meta-thesis}} N_5^+N_3^- \text{ or } N_5\text{-}N_3$$

characterization safety data → scale up → process improvement → production → testing



Make an alternative polynitrogen cation $N(N_3)_4^+$, $\cancel{Xe}N_3^+$, etc.

Make an alternative polynitrogen anion $N(N_3)_2^-$, etc.

Make $N(N_3)_3$

Cryogenic Solid HEDM Propellants

Use a solidified fuel or oxidizer as a storage medium for energetic additives, obtaining density and specific-impulse improvements

Depositing certain atomic or molecular species in solid hydrogen at 5% concentrations can increase specific impulse by more than 20%

Vehicle	Propellant	Payload Mass (lb)	Payload (lb) With 10% Density Increase	Payload (lb) With 10% Isp Increase	Payload (lb) With 10% Increase in Both
Rockwell SSTO RLV	LH2/LOX (Isp = 455 s)	40,000	51,200 **(+28%)**	68,000 **(+70%)**	76,800 **(+92%)**

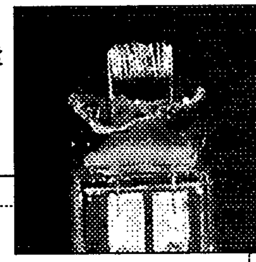
Large payload increases are achievable with modest density or specific impulse increases

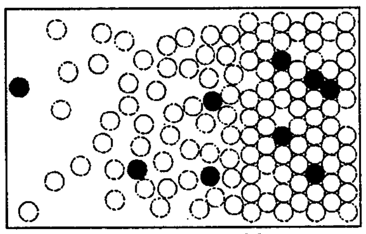
Cryogenic Solid HEDM Propellants

KEY ISSUES

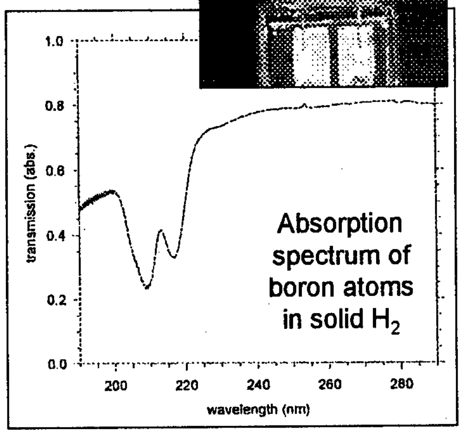
- Determine reactivity, diffusion, and recombination propensities to identify the most stable additives
- Develop and characterize high-flux sources of desirable HEDM additives
- Develop methods to characterize thick cryogenic solids with high additive concentrations

Boron filament source





Schematic of the deposition process



Absorption spectrum of boron atoms in solid H_2

Cryogenic Solid HEDM Program Plan

Planned FY99	Accomplished FY99	Planned FY00
Develop characterization method for sources of HEDM dopants	Time-of-flight mass spectrometer-based apparatus designed, constructed and tested	Use the new apparatus to characterize and optimize HEDM sources
Design a source high-flux, robust, pure source of boron atoms	Several designs considered; preliminary testing of boron cannon	Characterize and optimize the boron cannon; investigate e-beam and laser heating of boron
Develop diagnostic for determining concentration of arbitrary HEDM dopants in solid H_2	Method based on induced infrared activity in cryogenic solid hydrogen developed	Continue calibration of this technique by trapping known concentrations of various species in solid H_2
Develop means to calculate potential-energy surfaces for condensed-phase systems	Theoretical development of Spectral Theory of Schrödinger Eigenstates essentially completed	Begin implementation of the theory as a computationally viable methodology

A Sound Approach To A Vital Technology

"The highest leverage technology area impacting launch vehicles is the development of high-energy-density materials for use as propellants." – New World Vistas Panel on Space Technology (1995)

"The launch community will continue to rely on chemical rocket propulsion for the foreseeable future. Technology breakthroughs in propellant performance, density, and affordability will be crucial." – Breakthrough Technologies to Meet Future Air and Space Transportation Needs and Goals (National Academy of Sciences, 1998)

"The High Energy Density Material effort is based on a good science foundation. The work is well focused ... The overall approach from initial modeling, prototype synthesis, to production synthesis demonstrates excellent understanding of technology creation and delivery." – USAF Scientific Advisory Board Quality Review (1999)

The HEDM Program: Turning the Dreams of Yesterday into the Reality of Tomorrow

The HEDM effort is working on important problems in propellant development

HEDM propellants continue to be identified as a military-critical technology, and the AFRL HEDM program continues to be highly regarded

The PRSP HEDM group has identified key scientific issues in each area and is working to resolve them

Significant progress is being made on the key issues in each area of propellant development

The AFRL group guides AFOSR in selecting contractors to supplement and complement the in-house program

"The dream of yesterday is the hope of today and the reality of tomorrow."
– Robert Goddard (1904)